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(19)

(54) RAPIDLY-HARDENABLE RESIN AND USE THEREOF

(71) We, SIKA AG VORMALS KASPAR WINKLER & CO., a Swiss Company of Tüffenwies 16.22, Zürich, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns improvements in rapid-hardening resins of the type comprising an epoxide resin and an amine hardener.

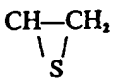
Cold hardenable mixtures of epoxide resins and amines, preferably polyamides containing amino groups have been used for a considerable time in the construction industry as coating substances, coverings, mortar, adhesive, injection agent and for impregnation purposes.

The hardening time of such mixtures, in other words the time required for the mixtures to reach a condition where they can be used is dependent upon temperature. Generally, the hardening reaction at temperatures beneath about 8°C proceeds so slowly that such mixtures can no longer be employed.

It has already been proposed to add to such hardenable mixtures, compounds which accelerate the hardening reaction.

A disadvantage of this proposal is that the accelerator, which is not consumed during the hardening reaction, unfavourably affects the properties of the hardened mixture, for example, the surface hardness, the resistance against the effects of water and chemicals and the mechanical strength, and thus such accelerators can only be added in limited quantities. Hence, the possibility of using the hardenable mixture containing the accelerator is limited to temperatures above about 5°C, and furthermore, since most of the accelerators are toxic soluble compounds, it should be apparent that epoxide resins containing accelerators generally cannot be used in the construction of swimming pools or drinking water installations. It is therefore an object of the present invention to provide a rapidly hardening synthetic resin which substantially overcomes the aforementioned drawbacks and limitations.

According to the present invention we provide a curable epoxy resinous composition comprising an epoxide resin, an amine hardener and as an accelerator an episulphide compound or compounds, the episulphide compound or compounds having on the average more than one



group per molecule and an apisulphide value in the range of 0.2 to 0.9 and the ratio of the epoxide resin to the episulphide compound or compounds being selected so that the resin composition hardens in the temperature range of –30°C to +10°C. As used hereinafter the term "episulphide value" indicates the number of equivalents of episulphide sulphur per 100 gms.

Preferably the episulphide compound or compounds has an episulphide value in the range of 0.5 to 0.9 The episulphide compounds markedly accelerate the hardening of epoxide resins by means of amine hardeners at low temperatures as a function of their dosage.

Preferably the episulphide compound or compounds comprises from 10 to 30% by weight of the total weight of the epoxide resin and the episulphide compound or compounds.

The episulphide compounds of the present invention are characterised by the features that they, together with amines at a temperature of 20°C. gell and harden within one minute.

The amines which are preferred for the hardening of such apisulphide compounds are aliphatic or cycloaliphatic amines, preferably diethylene triamine (DETA) triethylene tetramine (TETA) or tetraethylenepentamine (TEPA) which can be employed alone or in a mixture with other polyamines or polyaminoamides which may contain substituted aryl-or substituted aryl alkyl-residues.

The episulphide compounds or mixtures of episulphide compounds used according to the invention can be produced, for instance, according to the process which has been patented in DRP No. 636, 708 (German Reichspatent 636,708) in 1934 and discovered by K. Dachlauer and L. Jackel, from epoxide compounds by reaction with thiocyanates, sodium thiosulphate, thio-urea or by reduction of chloropolysulphides with Al-amalgam (French patent 1,428,686).

The episulphide groups of the episulphide compounds can possibly be bound by heteroatoms, especially oxygen, or functional groups, such as ester-, urea-, urethane-, or amide-groups or aliphatic-, cycloaliphatic-, possibly substituted aryl- or possibly substituted aryl-alkyl- residue.

It has been found from kinetic tests that polyepisulphide compounds initially react with polyamines and that the reaction products formed by such reactions either react with other polyepisulphide molecules or with polyepoxide molecules, and such reaction proceeds quicker than the reaction between a polyepoxide compound and a polyamine.

It is therefore possible to previously admix any given amine hardener, for instance an aliphatic or a cycloaliphatic amine or mixture of such amines such that the stoichiometric conditions are maintained, and to add the episulphide compound to the epoxide resin prior to mixing of the components, in such a dosage that there is obtained a hardenable mixture which at certain temperature possesses the processing time and hardening time respectively, for the intended purpose of use. In this way it is possible to control the degree of the hardening acceleration by means of the dosing of the episulphide compound throughout the temperature range of −30°C to +10°C.

Since the episulphide compounds are themselves consumed during the hardening reaction, producing insoluble products, the rapid hardening resins or resin mixtures of the present invention fulfil the regulations concerning toxicity.

The mixtures of epoxide resins with episulphide compounds can be employed with or without added substances or additives, such as fillers, pigments, plasticizers, extenders and auxiliary substances or adjuvants, such as surface-active agents, levelling agents, wetting agents, delustering or dulling agents, for instance as paint coats, coatings, coverings, adhesive, mortar or injection agent.

They are particularly suitable for processing with a so-called two-component or dual-component installation which separately conveys the resin components and the hardener components, for instance in injection processes, and reinforcing materials such as fabrics or fibres can be employed.

The invention will be further explained on the basis of the following examples. Testing of the Brinell hardness was undertaken in accordance with the procedures of DIN 50351 (the symbol DIN representing German Industrial Standards).

EXAMPLE 1.

The following Table 1 shows the accelerating influence of an episulfide compound upon the hardening of an epoxide resin of the bisphenol A-type by means of an amine hardener. The mixing ratio of resin:hardener is 4:1 parts by weight, the amine hardener contains 10% by weight triethylenetetramine (TETA) and the resin component contains the quantities of episulfide compounds, having an episulfide value of 0.78, shown in Table 1 below.

TABLE 1

	Inventive Mixture				Without Episulfide Compounds			
Resin component (parts by weight)	80	80	80	80	80	80	80	80
Amine Hardener (parts by weight)	20	20	20	20	20	20	20	20
Episulfide compound (parts by weight)	20	20	20	20	–	–	–	–
Temperature (°C)	+10	+5	0	–5	+10	+5	0	–5
Processing Time (minutes)	8	12	15	30	120	600	∞	∞

Example 2.

The following Table 2 illustrates the influence of the dosing of episulfide compound in Table 1 upon the hardening speed of the resin-hardener-mixture employed in Table 1. The amine hardener contains 10% by weight TETA.

TABLE 2

Episulfide compound (parts by weight)	30	20	15	10
Temperature (°C)	0	0	0	0
Processing Time (minutes)	8	15	18	30

Example 3.

The following Table 3 illustrates the influence of the dosing of the dimthylene-triamine (DETA) upon the hardening speed of the resin-amine hardener mixture used in Table 1, wherein the resin component contains 10% by weight of an episulfide compound having an "episulfide value" of 0.60 and the hardener component contains the quantities of DETA (% by weight) given in Table 3.

TABLE 3

DETA	5	8	10	12
Temperature (°C)	5	5	5	5
Processing Time (minutes)	28	20	15	12

Example 4.

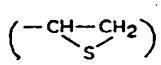
The following Table 4 illustrates the development of the Brinell hardness at a temperature of 10°C and –5°C for a non-accelerated and an accelerated resin-hardener-mixture. The non-accelerated mixture comprised a 100 g mixture of an aliphatic epoxy resin (formed by reacting glycerol and epichlorohydrin) and an amine hardener in a ratio of 3:1. The accelerated mixture comprised a similar 100 gm. mixture but in which the epoxide resin contained 25% by weight of the episulfide compound of Table 1 and the accelerated resin component contained 15% by weight TETA.

TABLE 4

Temperature (°C)	10			−5		
Brinell Hardness (kp/cm^2) after hour	10	50	100	10'	50	100
Accelerated	360	1180	1250	230	780	1050
Non-Accelerated	20	93	220	±0	±0	±0

WHAT WE CLAIM IS:—

1. A curable epoxy resinous composition comprising an epoxide resin, an amine hardener and as an accelerator an episulphide compound or compounds, the episulphide compound or compounds having on the average more than one



group per molecule and an episulphide value in the range of 0.2 to 0.9 and the ratio of the epoxide resin to the episulphide compound or compounds being selected so that the resin composition hardens in the temperature range of −30°C. to +10°C.

2. A composition according to claim 1 wherein the episulphide compound or compounds has an episulphide value in the range of 0.5 to 0.9 episulphide equivalents per 100 gms.

3. A composition according to claim 1 or claim 2 wherein the episulphide compound or compounds comprises from 10 to 30% by weight of the total weight of the epoxide resin and the episulphide compound or compounds.

4. A composition according to any one of the preceding claims wherein the amine hardener comprises an aliphatic or cycloaliphatic polyamine.

5. A composition according to any one of the preceding claims wherein the amine hardener includes any one of diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), or mixtures of DETA, TETA or TEPA.

6. A composition according to any one of the preceding claims wherein the epoxide resin is a diglycidyl ether of bisphenol A.

7. A composition according to any one of the preceding claims including any one of the following additives: surface active agents, levelling agents, wetting agents, delustering or dulling agents, fillers, pigments, plasticizers, extenders.

8. A curable epoxy resinous composition substantially as hereinbefore described with reference to the accompanying examples 2 and 3 and to the accelerated compositions of examples 1 and 4.

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